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Adhesion to zirconia as a function of primers/silane coupling agents, luting cement types, aging and test methods

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Adhesion to zirconia as a function of primers/silane coupling agents, luting cement types, aging and test methods

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ABSTRACT

This study evaluated the adhesion of resin cements to zirconia with different primers/silane coupling agents using two test methods with and without aging. Zirconia discs (Cercon) (N = 900, n = 15 per group) were ground finished to 2000 grit silicone carbide and randomly divided into seven groups: (a) C: No treatment (Control), (b) SG: Signum, (c) CL: Clearfil Ceramic Primer, (d) AP: Alloy Primer, (e) Monobond Plus, (f) ES-R: ESPE-Sil after Rocatec and (g) ES-C: ESPE-Sil after CoJet. Methacrylate (Variolink II-VL) and MDP based (Panavia F2.0-PN) dual-polymerized and self-adhesive resin cements (RelyX Unicem-RX) were adhered and polymerized accordingly. The specimens were further randomly divided into two groups to be tested after (a) 24-h dry storage at 37 °C and (b) thermocycling (×5000, 5–55 °C). Macroshear (MSB) and macrotensile bond tests (MTB) were conducted in an universal testing machine (crosshead speed: 1 mm/min) and failure types were analyzed after debonding. Data were analyzed using Univariate analysis and Tukey's tests (α = 0.05). Two-parameter Weibull modulus, scale (m) and shape (0) were calculated. While primer/silane ($p < 0.001$), cement type ($p < 0.001$) and aging ($p < 0.001$) significantly affected the bond results, test method did not show significant difference ($p = 0.237$). In MSB test, Weilbul moduli were more favorable for MP-VL (4.2) and AP-PN (6) combinations and after aging for MP-VL (4.2) and AP-PN (5.66). In MTB test, after aging, Weilbul moduli were more favorable for AP-PN (5.41). Bond strength results mostly decreased with SG (24–92%) after aging. Cohesive failures in the cement were more frequent with PN (252) compared to VL (83).

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Introduction

Ytrium-stabilized polycrystalline zirconia (hereafter: zirconia) offers a wide variety of clinical applications, such as full coverage single crowns, fixed-dental prosthesis (FDPs), resin-bonded FDPs, root posts or implant abutments in reconstructive dentistry. Zirconia has the most favorable properties compared to other high-strength ceramics having flexural strength of 900–1200 MPa, fracture resistance of more than 2000 N and fracture toughness

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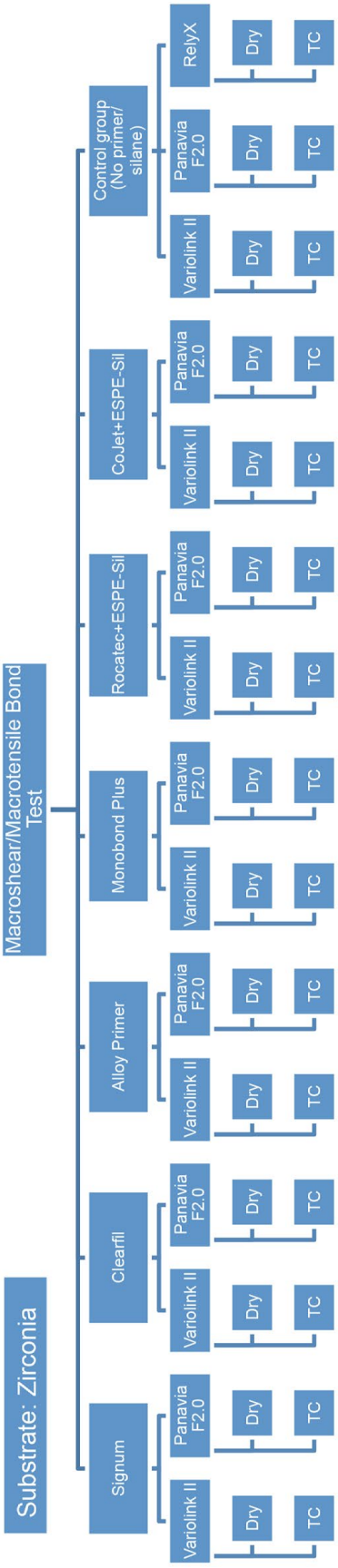

Figure 1. Allocation of experimental groups based on the primer/silane coupling agents, resin luting cements, aging and test methods.

of 9–10 MPa/mm^2, which is almost twice the value obtained for alumina-based materials and almost three times the value demonstrated by lithium disilicate-based ceramics.[1] With the advances in adhesive promoters, indication of resin-bonded minimal invasive restorations could be considered as an integral part of reconstructive dentistry. In that respect, not only the strength of the restorative material but also the adhesion of resin-based luting cements both to the dental tissues and the particular restorative material is of importance for the long-term clinical success.[2,3] This aspect becomes even more important when retention of FDPs does not rely on macromechanical principles as in the case of resin-bonded surface-retained or cantilever FDPs.[2,3]

Although etching with hydrofluoric acid and subsequent silanization of the cementation surface of glassy matrix ceramics is an efficient method to achieve durable adhesion of resin-based materials,[4,5] neither etching with hydrofluoric or other acids nor applying silane coupling agents resulted in adequate resin bond to zirconia [4,6–10] since such ceramics do not contain a silicon dioxide (silica) phase. For this reason, in order to enhance the adhesion of luting cements to oxide-based ceramics, during the last two decades, a number of surface conditioning methods have been suggested.[10] While some of these methods facilitate resin-ceramic bonding micromechanically employing airborne particle abrasion with alumina particles,[8,10] others are based on physicochemical activation of the ceramic surfaces using silica-coated alumina particles ranging in size from 30 to 250 μm followed by silanization [5,10,11] or chemical activation with functional monomer containing cements. [10,11] Among all conditioning methods, particle deposition methods deliver the most favorable adhesion, but they may have detrimental effect on the treated zirconia surface creating microcracks, thereby reducing its strength.[12,13] Unfortunately, surface roughening of zirconia with air-abrasion methods alone is also not sufficient for the adhesion of resin cements.[4] Additional chemical adhesion needs to be achieved using various silane coupling agents, primers and/or luting agents based on phosphate ester monomer 10-methacryloyloxydecyl dihydrogenphosphate (10-MDP), 4-methacryloxyethyl trimellitic anhydride (4-META), thiophosphoric acid methacrylate (MEPS) that can chemically react with oxides on zirconia.[14–16] However, all these cements or adhesion promoters still require air-abrasion in order to achieve a clean surface prior to their application according to the manufacturers.

Since the use of conventional resin cements is usually technique sensitive, and each ceramic type requires a different conditioning method, self-adhesive cements were introduced with the aim of simplifying clinical procedures and replacing the sensitive, multistep procedures during cementation. The material is applied directly on the dentin surface, without any necessity for pretreatment neither on the dentin, nor on the restorative material surface.[17] When self-adhesive resin cements or etching methods deliver comparable results to air-abrasion methods, possible hazards of particle deposition on zirconia could be eliminated. Likewise, since concerns exist on the possible damage created by the air-abrasion methods,[12,13,18,19] attempts have been made to promote primers based on organophosphate/carboxylic acid monomers specific for zirconia with which aggressive conditioning methods could be eliminated.[15,20] Unfortunately, hydrolytic stability of such primers is still of concern.[14,21,22]

Adhesive joints are subjected to both shear and tensile form of forces during chewing. The objectives of this study, therefore, were to evaluate the adhesion of dual-polymerized and self-adhesive resin cements to zirconia in conjunction with different primers and silane

coupling agents using shear and tensile adhesion test methods with and without aging and to evaluate the failure types after debonding. The null hypotheses tested were that bond strength results would not show significant difference depending on the primer/silane, cement type and aging and the test methods.

Materials and methods

Specimen preparation

The brands, chemical compositions, manufacturers and batch numbers of the materials used in this study are listed in Table 1.

Zirconia specimens (N = 900) (Cercon, Degudent, Hanau-Wolfgang, Germany) were prepared according to the manufacturer's recommendations (diameter: 10 mm; height: 2 mm). The specimens were wet ground finished using silicone carbide papers in sequence (# 400, 600, 800, 1200, 1500, 2000) for 30 s each. After sintering, the specimens were cleaned ultrasonically (Vitasonic, VITA Zahnfabrik, Bad Säckingen, Germany) in distilled water for 10 min. Specimens were then embedded in plastic molds (diameter: 12 mm, height: 10 mm) using autopolymerized polymethylmethacrylate (Scandiquick, Scandia, Hagen, Germany), keeping the upper surface free for bonding purposes using a device that maintained the specimens parallel to the X-axis. The specimens were then randomly divided into seven groups to be conditioned:

Surface conditioning methods

Group C:

This group received no primer/silane on the specimen surfaces and acted as the control group.

Group SG:

After mixing two components at 1:1 ratio, specimen surfaces were coated with one layer silane based on 10-MDP with acetone solvent (90%) (Signum Zirconia Bond I + II, Hereaus Kulzer, Hanau, Germany) using a clean brush for every specimen and left to react for 60 s. The specimens were placed in a polymerization unit (Heraflash, HiLite power, Hereaus Kulzer) for 90 s to accomplish further silane reaction according to the manufacturer`s instructions.

Group CL:

Primer and bond were mixed at 1:1 ratio, and specimen surfaces were coated with one layer silane based on 3-methacryloxypropyl trimethoxysilane coupling agent, γ-MPS (Clearfil SE Bond with Clearfil Porcelain Bond Activator, Kuraray, Tokyo Japan) with ethanol solvent (80%) using a clean brush for every specimen, gently air-thinned with oil-free air. The surface was then photopolymerized using an LED unit (Bluephase G2, Ivoclar Vivadent) for 10 s.

Group AP:

Specimen surfaces were coated with one layer silane based on 10-MDP and vinyl (Alloy Primer, Kuraray) with acetone solvent (90%) using a clean brush for every specimen and left to react for 1 min.

Table 1. The brands, abbreviations, manufacturers, chemical compositions and batch numbers of the materials used in this study.

Brand	Manufacturer	Chemical composition	Batch number
Primers/Silane coupling agents			
Signum Zirconia Bond I+II (SG)	Heraeus Kulzer, Hanau, Germany	Monomer: 10-methacryl-oxydecyldihydrogenphosphate 0–5% Solvent: acetone (>90%), ethanol (<1%)	010062 010657
Clearfil SE Bond and Clearfil Porcelain Bond activator (CL)	Kuraray, Tokyo, Japan	Monomer: 3-trimethoxysilylpropylmethacrylate (<5%) Solvent: ethanol (80–100%)	Primer: 00943A Bond: 01397A
Alloy Primer (AP)	Kuraray	Monomer: 6-(4-vinylbenzyl-N-propyl) amino-135-triazin-24-dithion, 10-methacryloyloxydecyl-dihydrogenphosphate solvent: acetone (>90%)	00359A
Monobond Plus (MP)	Ivoclar Vivadent, Schaan, Liechtenstein	Monomer: <1.5% Methacrylate, Phosphoric acid ester Solvent: Ethanol (96%)	M2 4811
ESPE-Sil (ES)	3 M ESPE, St. Paul, USA	Monomer: ethyl alcohol, 3-methacryloxypropyltrimethoxysilane solvent: >90% ethanol	
Resin luting cements			
Variolink II (VL)	Ivoclar Vivadent	bis-GMA, UDMA, TEGDMA, BPO, camphorquionine, barium glass, ytterbium trifluoride, Ba–Al fluorosilicate glass, spheroid mixed oxide Particle size: 0.04 - 3 µm (mean: 0.7 µm), Filler load (base: 73.4 wt%), Filler load (catalyst high viscosity: 77.2 wt%)	J 17818
Panavia F2.0 (PN)	Kuraray	Paste A: 10- Methacryloyloxydecyl dihydrogen phosphate Paste B: hydrophobic aromatic dimethacrylate, hydrophilic aliphatic methacrylate, hydrophilic aliphatic dimethacrylate-silanated barium glass filler (wt%)	00443 A 00221 B
RelyX Unicem Aplicap (RX)	3 M ESPE	Water (30–40%), copolymer of acrylic and itaconic acid (30–40%), 2-Hydroxyethyl methacrylate (25–35%)	38266
Particle type			
Rocatec (R)	3 M ESPE	110 µm Al_2O_3 particles (Rocatec-Pre) 110 µm silica-coated Al_2O_3 particles (Rocatec-Plus)	11520
CoJet (C)	3 M ESPE	30 µm aluminum oxide particles coated with silica	105

Group MP:

Specimen surfaces were coated with one layer silane based on 10-MDP and γ-MPS (Monobond Plus, Ivoclar Vivadent, Schaan, Liechtenstein) using a clean brush for every specimen and left to react for 1 min. The surfaces were then gently air-thinned with oil-free air.

Group ES-R:

In this group, specimen surfaces were initially airborne particle abraded in a laboratory air-abrasion device using tribochemical silica-coating system (Rocatec system, 3 M ESPE AG, St. Paul, USA). The specimens were first air-abraded with 110 μm Al_2O_3 particles (Rocatec-Pre, 3 M ESPE) followed by 110 μm silica-coated Al_2O_3 particles (Rocatec-Plus, 3 M ESPE) perpendicular to the surface from a distance of approximately 10 mm for a period of 15 s at 2.8 bar pressure. After drying the surface with oil-free air, the conditioned substrates were coated with γ-MPS silane with ethanol solvent (90%) (ESPE-Sil, 3 M ESPE) using a clean brush for every specimen and left to react for 1 min.

Group ES-C:

The specimens were air-abraded with 30 μm aluminum oxide particles coated with silica (CoJet Sand, 3 M ESPE) at 2.8 bar pressure from a distance of approximately 10 mm from the surface, in a circular motion for 15 s using an intraoral air-abrasion device (Dento-Prep, RØNVIG, Daugaard, Denmark). After drying the surface with oil-free air, the conditioned substrates were coated with silane as described in group ES-R.

Adhesive procedures

The primed and silanized specimens in each group were further divided into two groups depending on the two dual-polymerized luting cements based on methacrylate (VL, Variolink II, Ivoclar Vivadent) and 10-MDP monomer (PN, Panavia F2.0, Kuraray) to be bonded to the specimens. Separate groups of specimens from Group C received self-adhesive resin cement (RX, RelyX Unicem Aplicap, 3 M ESPE) that was activated in the corresponding mixer (Rotomix, 3 M ESPE) for 10 s.

One calibrated operator carried out adhesive procedures throughout the experiments. Translucent polyethylene molds (height: 4 mm, diameter: 3 mm) were stabilized on the ceramic specimens in a custom-made device. Base and catalyst paste of dual-polymerized resin cements were mixed in a 1:1 ratio on a mixing pad for 10 s. The mold was filled with the resin cement, a metal pin was inserted to ensure 100 μm cement thickness at the first layer of cement and it was photo-polymerized using an LED unit (Bluephase G2, Ivoclar Vivadent) for 40 s from five directions from a distance of 2 mm. Light intensity was assured to be higher than 1200 mW/cm^2, verified by a radiometer after every eight specimen (Model 100, Kerr, Orange, CA, USA). Oxygen-inhibiting gel (Oxyguard, Kuraray) was applied at the bonded margins and rinsed with cupious water after 1 min.

Polyethylene molds were gently removed from the test specimens. Half of the specimens were kept dry at 37 °C for 24 h in dark and the other half was subjected to thermocycling for 5000 cycles between 5 and 55 °C in distilled water (Haake DC 10, Thermo Haake, Karlsruhe, Germany). The dwelling time at each temperature was 30 s and the transfer time from one bath to the other was 10 s.

Macroshear and macrotensile tests

For the macroshear bond test (MSB), specimens were mounted in the jig of the universal testing machine (Zwick ROELL Z2.5 MA 18-1-3/7, Ulm, Germany) and the shear force was applied using a shearing blade to the adhesive interface until failure occurred. The load was applied to the adhesive interface as close as possible to the surface of the substrate at a crosshead speed of 1 mm/min and the stress–strain curve was analyzed with the software program (TestXpert, Zwick ROELL, Ulm, Germany). For the macrotensile bond test (MTB), specimens were mounted in the corresponding jig and resin cement disc was pulled with a grip from the zirconia surface at a crosshead speed of 1 mm/min.

Microscopic examination and failure analysis

After adhesion tests, debonded specimen surfaces were examined in order to analyze the failure types using an optical microscope (Zeiss MC 80 DX, Jena, Germany) at ×50 magnification. Failure types were classified as follows: Score 1: adhesive failure at ceramic–cement interface with no cement remnants left on the substrate, Score 2: <1/3 cement left adhered on the substrate, Score 3: >1/3 cement left adhered on the substrate, Score 4: Cohesive failure within the substrate.

Statistical analysis

According to the two-group Satterthwaite *t*-test (SPSS Software V.20, Chicago, IL, USA) with a 0.05 two-sided significance level, a sample size of 15 in each experimental group was calculated to provide more than 80% power to detect a difference of 5 MPa between mean values. Kolmogorov–Smirnov and Shapiro–Wilk tests were used to test normal distribution of the data. As the data were normally distributed, Univariate analysis of variance was applied to analyze possible differences between the groups where the bond strength was the dependent variable and primer/silane types (seven levels: C, SG, CL, MP, AP, ES-R, ES-C), cement types (3 levels: two dual polymerized and one self adhesive), aging types (two levels: dry vs. thermocycle) and test method (two levels: macroshear vs. macrotensile) as independent variables. Due to significant differences between groups, multiple comparisons were analyzed using Tukey's, Bonneferroni and two-sided Dunnett-T *post hoc* tests. Maximum likelihood estimation without a correction factor was used for two-parameter Weibull distribution to interpret predictability and reliability of adhesion (Minitab Software V.16, State College, PA, USA). p values less than 0.05 were considered to be statistically significant in all tests.

Results

Debonded specimens during thermocycling were considered 0 MPa.

While primer/silane ($p < 0.001$), cement type ($p < 0.001$) and aging ($p < 0.001$) significantly affected the bond results, test method did not show significant difference ($p = 0.237$).

With the MSB (MPa) test, in both dry and aged conditions in nonsilanized C groups, VL did not bond on zirconia (0 MPa) (Table 2(a)). After aging, C groups of PN cement (9.7 ± 3.4) presented significantly higher mean bond strength results compared to other

cements (0 –6.3 ± 4.3) ($p < 0.05$). Except for ES-R and CL groups (8 ± 3.9), with all primer/silane types, in dry conditions within VL (10.2 ± 1.9 – 15.4 ± 6.2) and PN cement groups (10.2 ± 1.9 – 14.1 ± 2.9), no significant difference was noted ($p > 0.05$). After aging, PN showed no significant decrease (9.2 ± 4.9 – 14.2 ± 4.5) ($p > 0.05$) but in VL, only AP (13.8 ± 3.7) and MP (11.1 + 6.1) showed significantly higher results compared to those of other silanes (1 ± 0.4 – 9 ± 5.5) ($p < 0.05$). In MSB test, Weilbull moduli were more favorable for MP-VL (4.2) and AP-PN (6) combinations compared to other groups (2.26–3.03 and 2.5–5.26, for VL and PN, respectively) and after aging for MP-VL (4.2) and AP-PN (5.66).

With the MTB (MPa) test, in both dry and aged conditions in nonsilanized C groups, VL either did not bond (0 MPa) or showed low (6 ± 5) bond strength to zirconia (Table 2(b)). In dry conditions, AP-VL (15.7 ± 4.9) and MP-VL (19.6 ± 4.7) and all silanes (12.1 ± 2.3 – 13.3 ± 1.6) except SG (4.4 ± 3.8) with PN showed significantly higher mean bond strength within each cement group ($p < 0.05$) (Table 2(b)). After aging, SG silane with both VL and

Table 2 (a). The mean macroshear bond strength values (MPa ± standard deviations), Weibull parameters (shape and scale), distribution and frequency of failure types per experimental group analyzed after bond strength test: Score 0: Adhesive failure at ceramic–cement interface with no cement remnants left on the substrate, Score 1:<1/3 cement left adhered on the substrate, Score 2:>1/3 cement left adhered on the substrate. The same superscript lowercase letters in the same column indicate no significant differences for cement-dry and uppercase letters for cement-thermocycle combinations ($p < 0.05$). For group descriptions see Table 1.

					Weibull parameters		Failure type distribution *n* (%)		
Group	Primer/ silane	Resin cement	Aging	Macroshear bond strength (Mean ± SD)	Shape	Scale	Score 0	Score 1	Score 2
1	SG	VL	Dry	12 ± 4.2^{a}	3.03	88.24	15 (100)	0 (0)	0(0)
2	CL	VL	Dry	15.4 ± 6.2^{a}	2.76	114.50	15 (100)	0 (0)	0 (0)
3	AP	VL	Dry	15 ± 3.8^{a}	3.2	87.27	15 (100)	0(0)	0 (0)
4	MP	VL	Dry	11.9 ± 3.7^{a}	4.2	108.58	15 (100)	0 (0)	0 (0)
5	ES-R	VL	Dry	8 ± 3.9b	2.26	59.55	13 (87)	2 (13)	0 (0)
6	ES-C	VL	Dry	12.3± 5.2^{a}	2.59	91.51	14 (93)	1 (7)	0 (0)
7	SG	PN	Dry	10.3 ± 4.8^{a}	2.5	76.91	15 (100)	0 (0)	0 (0)
8	CL	PN	Dry	14.1 ± 2.9^{a}	5.26	100.69	3 (21)	12 (79)	0 (0)
9	AP	PN	Dry	10.2 ± 1.9^{a}	6	72.54	5 (35)	10 (55)	0 (0)
10	MP	PN	Dry	10.6 ± 3.9^{a}	3.66	77.96	3 (21)	12 (79)	0 (0)
11	ES-R	PN	Dry	12.5 ± 4^{a}	3.46	91.9	11(72)	3 (21)	1 (7)
12	ES-C	PN	Dry	13.3 ± 3.1^{a}	4.98	95.34	15 (100)	0 (0)	0 (0)
13	C	VL	Dry	0^{b}	1.93	55.71	15 (100)	0 (0)	0 (0)
14	C	PN	Dry	5.7 ± 1.7^{a,b}	3.89	41.69	15 (100)	0 (0)	0 (0)
15	C	RX	Dry	12.1 ± 5.2^{a}	2.55	90.40	15 (100)	0 (0)	0 (0)
16	SG	VL	TC	1 ± 0.4^{A}	1.07	2.2093	15 (100)	0 (0)	0 (0)
17	CL	VL	TC	4.4 ± 1.7^{A}	2.67	32.312	5 (35)	10 (65)	0 (0)
18	AP	VL	TC	11.1 ± 6.1^{B}	2.04	100.04	15 (100)	0 (0)	0 (0)
19	MP	VL	TC	13.8 ± 3.7^{B}	4.2	83.34	15 (100)	0 (0)	0 (0)
20	ES-R	VL	TC	9 ± 5.5^{B}	1.8	67.43	15 (100)	0 (0)	0 (0)
21	ES-C	VL	TC	5.4 ± 3.3^{B}	1.86	40.59	15 (100)	0 (0)	0 (0)
22	SG	PN	TC	14 ± 4.9^{A}	3.2	103.22	8 (51)	7 (49)	0 (0)
23	CL	PN	TC	9.2 ± 4.9^{A}	2.11	69.55	12 (79)	3 (21)	0 (0)
24	AP	PN	TC	10.2 ± 2.2^{A}	5.66	72.94	11 (72)	3 (21)	1(7)
25	MP	PN	TC	9.5 ± 2.3^{A}	4.8	68.45	7 (49)	8 (51)	0 (0)
26	ES-R	PN	TC	14.2 ± 4.5^{A}	3.76	103.79	13 (86)	2 (14)	0 (0)
27	ES-C	PN	TC	11.5 ± 3.8^{A}	3.32	84.58	13 (86)	2 (14)	0 (0)
28	C	VL	TC	0^{B}	4.51	82.06	15 (100)	0 (0)	0 (0)
29	C	PN	TC	9.7 ± 3.4^{A}	3.06	71.81	7 (49)	8 (51)	0 (0)
30	C	RX	TC	6.3 ± 4.3^{B}	0.6	13.18	15 (100)	0 (0)	0 (0)

Table 2 (b). The mean macrotensile bond strength values (MPa ± standard deviations), Weibull parameters (shape and scale), distribution and frequency of failure types per experimental group analyzed after bond strength test: Score 0: Adhesive failure at ceramic–cement interface with no cement remnants left on the substrate, Score 1:<1/3 cement left adhered on the substrate, Score 2:>1/3 cement left adhered on the substrate. The same superscript lowercase letters in the same column indicate no significant differences for cement-dry and uppercase letters for cement–thermocycle combinations ($p < 0.05$). For group descriptions see Table 1.

					Weibull parameters		Failure-type distribution *n* (%)		
Group	Primer/ silane	Resin cement	Aging	Macrotensile bond strength (Mean ± SD)	Shape	Scale	Score 0	Score 1	Score 2
1	SG	VL	Dry	10.3 ± 6.5^{a}	0.99	59.19	15 (100)	0 (0)	0 (0)
2	CL	VL	Dry	13.8 ± 4.1^{a}	3.93	100.46	0 (0)	0 (0)	15 (100)
3	AP	VL	Dry	15.7 ± 4.9^{b}	3.67	115.1	0 (0)	0 (0)	15 (100)
4	MP	VL	Dry	19.6 ± 4.7^{b}	4.53	141.74	1 (7)	0 (0)	14 (93)
5	ES-R	VL	Dry	7.1 ± 3.6^{a}	0.76	27.66	15 (100)	0 (0)	0 (0)
6	ES-C	VL	Dry	10.5 ± 4.8^{a}	1.29	63.37	15 (100)	0 (0)	0 (0)
7	SG	PN	Dry	4.4 ± 3.8^{a}	0.7	13.855	15 (100)	0 (0)	0 (0)
8	CL	PN	Dry	12.8 ± 4^{b}	2.09	85.53	0 (0)	0 (0)	15 (100)
9	AP	PN	Dry	13.3 ± 1.6^{b}	2.96	86.94	0 (0)	0 (0)	15 (100)
10	MP	PN	Dry	13 ± 3.7^{b}	3.89	94.61	0 (0)	0 (0)	15 (100)
11	ES-R	PN	Dry	12.7 ± 2.9^{b}	5.59	95.27	0 (0)	0 (0)	15 (100)
12	ES-C	PN	Dry	12.1 ± 2.3^{b}	2.7	79.91	0 (0)	0 (0)	15 (100)
13	C	VL	Dry	0^{a}	3.39	93.39	15 (100)	0 (0)	0 (0)
14	C	PN	Dry	7.2 ± 2.7^{a}	2.89	52.55	14 (93)	1 (7)	0 (0)
15	C	RX	Dry	12.5 ± 3.6^{b}	3.89	91.11	11 (93)	4(28)	0 (0)
16	SG	VL	TC	6 ± 5^{A}	0.68	9.237	13 (86)	2 (14)	0 (0)
17	CL	VL	TC	15.9 ± 4.4^{B}	2.56	94.81	0 (0)	0 (0)	15 (100)
18	AP	VL	TC	13.5 ± 3.7^{B}	2.02	76.21	0 (0)	0 (0)	15 (100)
19	MP	VL	TC	15.9 ± 3.3^{B}	4.04	84.23	0 (0)	0 (0)	15 (100)
20	ES-R	VL	TC	11.5 ± 4^{B}	1.56	73.23	0 (0)	0 (0)	15 (100)
21	ES-C	VL	TC	6.8 ± 3^{A}	5.25	92.22	15 (100)	0 (0)	0 (0)
22	SG	PN	TC	3.3 ± 2.5^{A}	0.52	14.639	15 (100)	0 (0)	0 (0)
23	CL	PN	TC	13 ± 3.7^{B}	0.55	5.691	0 (0)	0 (0)	15 (100)
24	AP	PN	TC	12.7 ± 2.6^{B}	5.41	113.58	1 (7)	0 (0)	14 (93)
25	MP	PN	TC	11.3 ± 3.9^{B}	3.6	115.97	1 (7)	0 (0)	14 (93)
26	ES-R	PN	TC	12 ± 2.5^{B}	4.79	97.89	1 (7)	0 (0)	14 (93)
27	ES-C	PN	TC	12.9 ± 3.4^{B}	3.38	84.76	0 (0)	0 (0)	15 (100)
28	C	VL	TC	0^{A}	*	*	15 (100)	0 (0)	0 (0)
29	C	PN	TC	9.7 ± 3.2^{A}	0.64	17.72	12 (79)	2(14)	1 (7)
30	C	RX	TC	10 ± 5.5^{B}	0.62	29.853	11 (72)	4 (28)	0 (0)

*$p < 0.05$.

PN showed significantly lower results (6 ± 5, 3.3 ± 2.5, respectively) ($p < 0.05$). In MTB test, Weilbull moduli were more favorable for MP-VL (4.53) and ES-R-PN (5.59) combinations compared to other groups (0.76–3.67 and 0.7–3.89, for VL and PN, respectively) and after aging for MP-VL (4.04) and AP-PN (5.41).

In all test and cement combinations, bond strength results decreased with SG from 24 to 92%.

After aging, cohesive failures in the cement were more frequent with PN (252 out of 450) compared to VL (83 out of 450) with both tests methods (Tables 2(a) and (b)).

Discussion

Based on the results of this study, except for test methods, since primer/silane, cement type and aging significantly affected the bond results, the null hypotheses tested could be partially rejected.

A number of test methods have been suggested to study adhesion of resin-based materials to zirconia (i.e. macroshear, microshear, macrotensile and microtensile tests). In order to measure the bond strength values between an adherent and a substrate accurately, it is crucial that the bonding interface should be the most stressed region, regardless of the test methodology being employed. Previous studies using stress distribution analyses have reported that some of the bond strength tests do not appropriately stress the interfacial zone.[22,23] Shear tests have been criticized for the development of nonhomogeneous stress distributions at the bonded interface, inducing either underestimation or misinterpretation of the results, as the failure often starts in one of the substrates and not solely at the adhesive zone.[22,23] Conventional tensile tests also present some limitations, such as the difficulty of specimen alignment and the tendency for heterogeneous stress distribution at the adhesive interface. On the other hand, when specimens are aligned correctly, the microtensile test shows more homogeneous distribution of stress, and thereby more sensitive comparison or evaluation of bond performances.[22] However, minute deviations in specimen alignment in the jig may cause increase bond strength due to shear component being introduced during debonding the adhered joints.[23]

During chewing function since adhesive joints are exposed to both shear and tensile forces, information on adhesion durability with both tests remains crucial when ranking the performance of silane–cement combinations. When one-to-one comparisons were made for each silane–cement combination, the test method did not show significant difference in mean bond strength results for both dry and aged conditions. One explanation for this finding could be the similar surface area of the bonded areas in both tests. The results obtained correspond to the ranges summarized in a recent meta-analysis with similar cements.[10] Especially with the MDP-based cement (PN), higher results were reported using the macrotensile test even in prolonged aged conditions.[8] However, it has to be noted that in those studies, cements were additionally polymerized in an oven under heat that was not practiced in this study as heat polymerization is neither manufacturer`s recommendation nor clinically relevant. Nevertheless, the results achieved are still much inferior than those reported for glassy matrix ceramics after etching with hydrofluoric acid and silanization.[4,5]

In this study, one methacrylate, one MDP–based cement and self-adhesive cement were used where the latter does not require conditioning the dentin or ceramic surfaces. Such cements contain multifunctional phosphoric acid dimethacrylate modified monomers in their chemical compositions.[17] As zirconia ceramic includes oxides, in principle, the surface conditioning with primers or resins having adhesive functional monomers such as phosphoric acid group monomer in their composition are expected to improve the bonding to zirconia. With MSB and MTB test methods, after aging conditions, drastic decrease was observed in bond strength of self-adhesive cement tested. Likewise, the incidence of adhesive failures with this cement was also very high. Thus, it cannot be stated that bifunctional monomers of self-adhesive cement was sufficient to establish durable bond solely with this cement on zirconia. Without any surface conditioning and silanization, long-term stability of self-adhesive cement tested (RX) could not be expected.[10] Similarly, without the use of

any primer/silane, methacrylate-based cement VL resulted in practically no bond strength already in dry conditions. On the contrary, some level of bonding could be achieved with MDP containing cement without the use of any primer/silane, but these results increased significantly when zirconia surface was treated with an MDP containing primer. In both test methods, supported also by favorable Weilbull moduli in PN-AP groups clearly indicate possible copolymerization between AP primer and the PN cement. Although the results were not as favorable as for AP-PN, with the MP-VL combination also increased results were obtained. MP silane containing both MPS and MDP possibly copolymerized on one side to zirconia with its MDP content, and on the other side to the mechacrylate resin cement with the MPS silane.[7,14,15] Yet, the results were not as favorable as AP-PN combination when bond strength, failure types and Weilbull moduli are considered. Hence, it could be stated that the compatibility of the primer/silane with the resin cement is decisive in durable adhesion to zirconia.

The polycondensation of bifunctional silane monomer with the general formula of (R–O–) 3-Si–O–R, R being the first and O–R the second silane functionality, can provide a highly cross-linked and reactive polyorganosiloxane layer on ceramics, also increasing the surface wettability.[14] Since they are prone to hydrolytic degradation,[14,21,22] attempts are being made to increase their crosslinking using other silanes [20] that could be further investigated after contamination. Nevertheless, hydrolysis of silane in water diminishes lifetime of adhesive joints.[14,21,22] When water molecules penetrate into the adhesive interface, existing physical bonds are destroyed and from the untreated surfaces cracks may initiate yielding to detachment of the resin-based materials.[14,21,22] In this regard, solvent evaporation represents a factor affecting the coupling potential of silanes.[24,25] Even though a small amount of solvent may help silane wetting, incomplete evaporation may impair adhesion. Water, alcohol, acetone, acetic acid and other by-products that remain on the surface, if not completely expelled by drying procedure, may remain as hydrogen-bonded to the OH-rich sites. This may decrease the number of bond sites available for reacting with silane, thus compromising the final degree of siloxane bond formation.[25] Accordingly, heat treatment process was suggested to evaporate the solvent and volatile by-products from the silane reaction, catalyzing and completing the condensation reactions both with the substrate and within the silane coating.[25] In this study, no heat treatment was applied to the silane layer in any of the groups except for SG which was required according to the manufacturer`s recommendations. Interestingly, however, although SG contains 10-MDP, significant decrease was noted after aging with both cements using the two test methods. This could relate to the less amount of MDP (0–5%) in the SG silane according to the manufacturer`s information. In order to minimize hydrolytic degradation effect, heat treatment on the other tested primers/silanes warrants further research.

Oral fluids are known to degrade ceramic–resin interfaces resulting in slow crack growth.[26] Testing the adhesive joints either after water storage or thermocycling yield to hydrolytic degradation at the interface and usually results in decreased bond strength of resin-based materials to zirconia.[7,27] Exceptionally, in the control group with PN, after both test methods, increase in bond strength was noted. Also, in some other groups, such as SG-PN and ES-R-PN, similar observations were made. This could be attributed to further polymerization of PN cement at the 55 °C during thermocycling. In future studies, aging effect after long-term water storage should be compared to thermocycling aging route.

One objective of this study was to find out whether application of primer/silanes alone could substirtute air-abrasion protocols where adhesion is achieved through micromechanical retention obtained with air-abrasion in part and the other as a consequence of chemical reaction with the silane coupling agent. During air-abrasion, since the energy available for crack propagation is in part dissipated in the damaged area shaped by the monoclinic zirconia, transformation toughening occurs in zirconia.[28] However, when the increase in volume exceeds the elastic limit of zirconia, it can promote the crack propagation, inducing new microcracks and even catastrophic fracture of the structure.[29] This mechanism could be influenced by several factors that act in an isolated or associated form, such as shape, size and location of grains, the presence of defects and/or oxygen vacancies in the structure, type and amount of stabilizing oxides, manufacturing methods, applied stresses and temperature variation.[30] Based on the results obtained in air-abraded groups given the particle deposition parameters, could be substituted with some primer/silane–cement combinations. Particle deposition duration in this study was 15 s according to the manufacturer`s instructions, but prolonged duration longer than 20 s could increase the amount of silica particles on the surface also increasing the bonding sites for the silane.[31] Nonetheless, prolonged particle deposition or increased pressure could at the same time increase the monoclinical phase in zirconia.[18,19]

Bond strength data should also be interpreted with failure types. While Score 1 represents the adhesive and therefore weak bond strength, Scores 2 and 3 indicate better adhesion to the substrate. The high incidence of mixed failures (Scores 2 and 3) supports the statement that PN cement bond better to zirconia than with VL. Interestingly, both cements showed higher incidence of mixed failures after MTB test than with MSB. By this type of failure type, the cohesive strength of the resin cement also plays a role and when the cohesive strength does not exceed that of the adhesive strength at the bonded interface, the cement fails cohesively itself. Thus, future studies should also consider cement composition when interpreting failure types especially in tensile test methods.

Recently, some chemical etching solutions such as CH_2CL_2 and those containing ferric chloride has been reported to dissolve the grain structure on the zirconia surface, enlarging the grain boundaries throughout the preferential removal of the less-arranged, high-energy peripheral atoms.[32] The results of this study, should be also compared with non-invasive etching protocols on zirconia.

Conclusions

From this study, the following could be concluded:

(1) Both 10-MDP and methacrylate cements tested profitted from the use of primers/silane coupling agents for improved adhesion to zirconia.
(2) Testing adhesion without aging through thermocycling did not result in significant difference between methacrylate and 10-MDP cement–silane combinations.
(3) After aging, 10-MDP cement with all silane combinations and methacrylate cement with AP and MP silanes showed significantly higher results compared to those of other silanes.
(4) In all tests and silane–cement combinations, bond strength results decreased the most with SG silane.

(5) After aging, Weilbull distribution indicated more reliable adhesion with AP-PN.
(6) Regardless of the test methods, after aging, cohesive failures in the cement were more commonly observed with 10-MDP cement compared to methacrylate or self-adhesive cements.

Clinical relevance

Considering bond strength values and the failure types, regardless of test method, 10-MDP-based dual-polymerized resin cement could be suggested as the choice of cement in conjunction with 10-MDP primer for more reliable adhesion to zirconia that could also as an alternative to air-abrasion protocols.

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Disclosure statement

The authors did not have any commercial interest in any of the materials used in this study.

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